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SELECTIVE REDUCTION OF NITRIC OXIDES WITH AMMONIA USING A CELLULAR BLOCK CATALYST

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An aluminum-vanadium cellular block catalyst for selective reduction of nitric oxides with ammonia has been developed. With an average degree of conversion of oxides over 90%, the efficiency of the proposed catalyst is significantly higher than that of industrial catalysts currently used. Such catalyst can be recommended for use in selective plants for purification of waste gases from nitric oxides, which makes it possible to significantly decrease the cost of making a catalyst block.

Selective catalytic reduction of nitric oxides to molecular nitrogen using ammonia is one of the main processes in purifying gaseous emissions from industrial enterprises. This is usually performed using granulated catalysts containing precious metals, as well as oxide systems of different types and shapes prepared by extrusion [1]. As a rule, such catalysts have low mechanical strength and are prone to substantial wear in the process. The history of development of catalysts includes powders, extrudates, tablets, granules, catalytically active metals and their oxides, and on to catalytic systems in the form of porous continuous blocks.

Block catalysts used for solving environmental problems are currently gaining wide acceptance due to their extended surface, ample selection of designs, low pressure difference, high thermal resistance and mechanical strength, and facile orientation in the reactor [2].

Block catalyst, as a rule, have a honeycomb or cellular structure and are intended for various chemical processes, from detoxication of gaseous emissions to liquid-phase catalytic processes in the synthesis of organic compounds.

Cellular catalysts have been recently upgraded by applying a highly porous active component on a block carrier with prescribed structural and strength parameters. The active components are oxide systems V – Ti – O and Cu – Ti – O, as well as metal-substituted zeolite ZSM-5 (Cu ZSM-5 and Co ZSM-5) [1].

To improve the thermal stability of the secondary oxide coating deposited for surface development, the modifying additives such as cesium zirconium, etc., are introduced, which also increases the resistance of the catalyst to toxins [3].

Such block oxide catalysts of the V – Ti – O system synthesized at the G. K. Boreskov Institute of Catalysis were

tested in the process of restoring nitric oxide with ammonia. A load on the catalysts (one of the main parameters of preparation efficiency) was equal to $0.018 \text{ g NO}_x / (\text{g}_{\text{cat}} \cdot \text{h})$ at a degree of conversion up to 90% [1]. In block cellular structure containing vanadium based on titanium oxide this parameter is lower.

The vanadium catalyst AVK-10 (aluminum-vanadium catalyst) used currently for reducing nitric oxide with a degree of conversion $\text{NO}_x \rightarrow \text{N}_2$ up to 90% shows that the catalyst load is approximately $0.01 \text{ g NO}_x / (\text{g}_{\text{cat}} \cdot \text{h})$.

The data are obtained in purifying gas flows from nitric oxide on the selective plant operating at the Ya. M. Sverdlov Works.

Catalyst AVK-10, while having high catalytic activity, has also substantial disadvantages. It is easily destroyed under the effect of the acid medium (nitric acid vapor) and its granules fuse to one other at temperatures of 220 – 250°C, which impairs the passage of a gas flow via the catalyst layer. Furthermore, charging and especially discharging granulated catalyst are extremely labor-consuming dirty processes. Therefore, our purpose was to search for a catalyst which, on the one hand, would be more active than the currently used catalysts and, on the other hand, would be free from the disadvantages typical of catalyst AVK-10.

For our research we selected a cellular block ceramic carrier with vanadium oxide (12 wt.% V_2O_5) deposited from a vanadyl sulfate solution using the impregnation method.

It is known that the use of highly porous cellular ceramics as catalyst carriers for various purposes offers advantages with respect to resistance to gas flow, degree of purification, simplicity of operation, and finally, cost effectiveness [4].

A cellular ceramic carrier was produced by depositing a material layer (metal oxides) on the surface of an organic structure-forming matrix from reticulated polyurethane foam

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TABLE 1

Quantity of NO _x , g/m ³		Degree of conversion NO _x → N ₂ , %	Load on catalyst, g NO _x /(g _{cat} · h)
input	output		
1.7	0.05	97.0	0.28
1.3	0.06	95.3	0.22
1.5	0.04	97.3	0.25
0.8	0.19	76.3	0.13
1.0	0.05	95.0	0.17

PPU-ÉO-100 (TU 6-05-5127-82) with subsequent sintering of this layer and removal of the matrix by thermal destruction (USSR Inventor's Certif. Nos. 577095 and 1366294).

The initial batch was electrocorundum with an additive of sintering-active disperse aluminum. The temporary technological binder for slip preparation was a PVA solution. Intermediate molded articles impregnated with slip after drying had high mechanical strength. Next, the dried articles were fired at 1550°C according to a special schedule ensuring preservation of sample integrity with low shrinkage (2–3%).

An additional extension of the surface was achieved by depositing 6–7 wt.% γ -Al₂O₃ on the cellular carrier.

The process of reduction of nitric oxide with ammonia was investigated in a flow-type reactor at 220–230°C for several days under the following conditions: catalyst volume 520 ml, catalyst weight 180 g, quantity of gases passing through the catalyst 30 m³/h.

The experimental flow-type reactor is a tube of 50 mm diameter installed in parallel with an industrial catalytic reactor filled with catalyst AVK-10. An experimental cellular block catalyst with a total length equal to the height of the catalyst ABK-10 layer (300 mm) was inserted into the experimental reactor. Owing to high porosity (approximately 85%), the flow rate of the gas mixture via the cellular catalyst was 30 m³/h, or 170 liters/(g_{cat} · h), which is significantly higher than the flow rate via the industrial catalyst AVK-10 (approximately 5.6 liters/(g_{cat} · h) with a porosity level of 30%.

In this context it could be expected that for a degree of conversion of NO_x to N₂ meeting the standard requirements (approximately 90%) the activity (catalyst load) of the experimental sample would be significantly higher than that of catalyst AVK-10.

The catalytic activity was estimated based on the degree of conversion of NO_x and the NO_x load on the catalyst in the

gas flow arriving to the selective plant for detoxication of nitric oxides at the Ya. M. Sverdlov Works.

The experimental data are listed in Table 1 (ammonia flow rate is about 60 liters/h).

It can be seen that for the average degree of conversion of NO_x equal to 92.2% the load on the catalyst was 0.21 g NO_x/(g_{cat} · h), which is 20 times higher than for catalyst AVK-10 and 10 times higher than for the oxide catalyst of the V–Ti–O system synthesized at the G. K. Boreskov Institute of Catalysis. These data corroborate the high activity of the cellular block catalyst.

The content of nitric oxides in the gas stream at the exit from the reactor in compliance with the technical requirements did not exceed 0.23 g/m³ and the ammonia content was 0.8 g/m³.

It is proposed in [5] to reduce nitric oxides with ammonia using a vanadium block catalyst on a metallic carrier made of aluminum foil. The degree of conversion of NO_x from waste gas is shown, but the gas concentration is not indicated; therefore, it is impossible to compare the quantitative load of nitric oxide on the catalyst. Furthermore, the process was performed at a temperature of 305°C, which is nearly 100°C higher than in real conditions.

Thus, the proposed cellular block aluminum-vanadium catalyst with respect to its activity in the reaction of reduction of nitric oxides significantly exceeds the catalyst used in industry and can be recommended for use at selective plants for purification of waste nitric oxide gases, which will significantly reduce the cost of making a catalyst block.

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